

ORIGIN OF CARBONATE IN MARTIAN METEORITE ALH 84001. E. R. D. Scott and A. N. Krot, Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu HI 96822, USA (escott@pgd.hawaii.edu).

Introduction: A significant argument advanced by McKay et al. [1, 2] in favor of a biogenic origin of the carbonates in ALH84001 was that abiogenic origins – both low and high temperature – appeared to be less plausible. However, subsequent shock studies have suggested that impact heating may have modified carbonates [3-7]. We inferred that plagioclase glass and rare silica grains formed from impact melts, and Raman spectroscopy [8] confirmed that plagioclase had been melted at $>1200^{\circ}\text{C}$ suggesting shock pressures exceeded 35-45 GPa. Morphological similarities between grains of plagioclase glass and irregularly shaped carbonates in fractures and the occurrence of intermixed grains in fractures suggested that carbonates may also have been shock heated so that a CO_2 -rich fluid was injected into cooler fractured pyroxene during shock decompression causing crystallization in seconds.

Types of carbonate: Carbonates in ALH84001 occur in three locations: a) disks, veins and irregularly shaped grains in healed fractures in pyroxene; b) massive grains and globules and smaller grains associated with plagioclase glass on pyroxene grain boundaries; and c) as generally equant grains that appear to poikilitically enclose pyroxene fragments in fracture zones (also called granular bands and crushed zones [9, 10]). McKay et al [1, 2] studied disk-shaped carbonates which are abundant on freshly broken surfaces; we studied all kinds of carbonates in polished thin sections. The close association of the three carbonate types and the uniformity of their chemical zoning trends on MgCO_3 - FeCO_3 - CaCO_3 plots show that all carbonates in ALH84001 formed by the same process [4, 11].

Origins of carbonate: Three different origins have been proposed for carbonates in ALH84001: a) biogenic or abiogenic precipitation from CO_2 -rich fluids that percolated through fractures at low temperatures [1, 12]; b) reaction between CO_2 -rich fluids and pyroxene, plagioclase or plagioclase glass at low or high temperatures [13, 14]; and c) shock heating and mobilization of preexisting carbonates [3-5]. Because voids are absent next to carbonates (except for fractures that postdate carbonate crystallization), grains in pyroxene crystals and plagioclase glass appear to have replaced the adjacent phase. However, replacement mechanisms are not plausible because phases rich in Si, Al, Na etc that form during such replacement reactions are

totally absent [14]. In addition, there should be compositional differences between carbonates in pyroxene and those in plagioclase, but none are observed. Carbonate grains in pyroxene could not have formed by replacement of plagioclase glass because carbonates are more abundant than glass in pyroxene, composite grains are rare, and glass grains are surrounded by radiating cracks whereas carbonates are not.

Carbonates in fractures: Studies of disks and veins in thin sections show that carbonate-bearing fractures were closed after carbonates had started to form so that unfilled portions of fractures were resealed around the carbonates. The concentration of planar defects around carbonate and plagioclase glass inclusions on fractures suggests that these fractures were closed by impact. If carbonates formed from externally derived fluids, chemical variations across carbonate grains would reflect external changes in fluid composition over time and fractures would have been closed after carbonate growth. However, if carbonates formed rapidly from impact-derived fluids, the chemical variations must reflect internal fractionation in trapped fluids, and fractures would have been closed during carbonate growth.

Several features favor crack closure during growth and internal control of chemical fractionation. The tapered edges of some carbonate disks and veins, the absence of deformation in the tapered rims of carbonate grains and the presence of well faceted magnesite rims favor crack closure during carbonate growth. Occurrences of magnesite at the enclosed end of carbonate-filled cracks are difficult to reconcile with late deposition from an externally derived fluid as the cracks would have been effectively sealed with early-formed Ca-rich carbonate. In addition, magnesite microdisks are found around some disks and veins but not elsewhere implying that chemical fractionation of the fluid was caused by carbonate crystallization. We infer that the magnesite microdisks formed from residual trapped fluid that was squeezed a short distance along the fractures as they closed. Carbonates in pyroxene fractures are heterogeneously distributed: heavily deformed pyroxene crystals around interstitial plagioclase glass can contain up to 5-10 vol. % carbonate consistent with limited transport of carbonate-rich fluids along fractures.

Studies of plagioclase glass and metal-troilite in heavily shocked L and E chondrites [15] show that

monomineralic melts of readily deformed minerals such as troilite and plagioclase are injected into fractures which were formed by shear stresses and then resealed during shock decompression. Grains of plagioclase glass and metal-troilite are heterogeneously distributed in healed fractures in pyroxenes as spheroids, sheets and irregularly shaped grains, like the carbonates in ALH84001. Metal grains are chemically zoned and form crystals $>100\text{ }\mu\text{m}$ in size because of rapid diffusion in metallic melts.

Carbonates in fracture zones: Fracture zones contain broken pyroxene crystals $5\text{--}100\text{ }\mu\text{m}$ in size that were formed from mm-cm-sized crystals by localized shear stresses, rotated $>20^\circ$ and squeezed together to remove voids. Fracture, rotation and compression occurred during impact(s). We and others [e.g., 11, 14], find no evidence for metamorphic equilibration of minerals after fracture zones were formed [9, 16]. Localized, brief frictional heating probably aided void removal. Fracture zones contain grains of carbonate and plagioclase glass that are sparsely distributed among the pyroxene fragments and are not fractured and deformed like the pyroxene showing that they formed after the pyroxene crystals were fragmented. Carbonates fill only a tiny fraction of the spaces that once existed between pyroxene fragments and could not have formed after the pyroxene fragments were squeezed together to remove voids. Carbonates must therefore have formed from fluids that were present between the pyroxene fragments when the fracture zones formed. Occurrences of aligned trails of plagioclase glass and chromite grains within fracture zones that lead to larger peripheral grains show that plagioclase was molten and chromite solid when the fracture zones formed by shear stresses. One large carbonate-plagioclase grain was also found with emanating parallel trails of carbonate and plagioclase glass grains [5]. Carbonate-pyroxene boundaries within large carbonate grains may be subhedral [3, 6], inconsistent with low temperature precipitation of carbonate in fractures. Carbonates and plagioclase glass in fracture zones both appear to have formed at high temperatures from impact-mobilized fluids which solidified as voids closed.

Carbonates mixed with plagioclase glass on pyroxene grain boundaries: Textures in these occurrences are highly varied and complex. However, the concentration of carbonate grains in fractured pyroxene around grain boundary carbonate-plagioclase glass intergrowths, implies that prior to impact heating, carbonates in ALH84001 were concentrated at interstitial sites together with plagioclase. Small amounts may also

have been distributed in fractures. The first carbonates could not have formed at high temperatures as burial depths of $>120\text{ km}$ at 900°C would have been needed to prevent carbonate and pyroxene from reacting to form CO_2 . The first carbonates probably crystallized instead from fluids at low-temperatures in voids formed by gas bubbles during the final stages of igneous crystallization. Carbonates in other martian meteorites probably formed this way, possibly as evaporite deposits. The presence of partly filled voids and adjacent plagioclase shock melts would have enhanced the shock heating of carbonates. Partial decomposition of carbonates by shock heating [6] without mobilization of shock-formed fluids appears less plausible as there is no correlation of chemical zoning with proximity to plagioclase melt.

Arguments against shock formation of carbonates: In some shock experiments [17], calcite appears to have been unaffected by shock pressures of 50 GPa. However, shock heating of minerals is heterogeneous and probably controlled by shear stresses. Thus shear stresses and matrix effects will be critical. Shock pressures in ALH84001 may also have exceeded 50-60 GPa. Chemical zoning in carbonates is not explained by this model. However, given our poor understanding of phase relations and kinetics at high T and P in the ternary carbonate system, it is not implausible that zoning resulted from fractionation between solid, melt and vapor. Impact melt pockets in heavily shocked rocks cool at diverse rates according to local conditions so that a unique crystallization sequence cannot be specified. Numerous generations of crosscutting melt veins and brecciation are observed in the floors of terrestrial craters so that many impacts [16] are not required to account for deformation features in ALH84001.

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